Statistical and Thermal Physics: Class Exam I

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Instructions

- There are 6 questions on 9 pages.
- Show your reasoning and calculations and always explain your answers.

Physical constants and useful formulae

$R = 8.31\,\text{J/mol K}$ $N_A = 6.02 \times 10^{23}\,\text{mol}^{-1}$ $k = 1.38 \times 10^{-23}\,\text{J/K}$ $1\,\text{atm} = 1.01 \times 10^5\,\text{Pa}$

Question 1

A quantity of air, a diatomic gas ($\gamma = 7/5$), initially occupies a volume of $2.0 \times 10^{-3}\,\text{m}^3$ at atmospheric pressure and at temperature 300 K. This is allowed to expand adiabatically, doubling its volume. Determine the pressure and temperature at the end of this process.

$$PV^\gamma = \text{Const} \quad : \quad P_iV_i^\gamma = P_f V_f^\gamma$$

$$\frac{P_i}{P_f} = \left(\frac{V_f}{V_i}\right)^\gamma, \quad \frac{P_i}{P_f} = \left(\frac{2V_i}{V_i}\right)^\gamma = \frac{P_i}{P_f} = (2)^\gamma \quad \therefore \quad P_f = \frac{P_i}{2^\gamma}$$

$$P_f = \frac{1.01\times10^5\,\text{Pa}}{2^{7/5}} = 38{,}272\,\text{Pa} \quad \boxed{P_F = 38{,}272\,\text{Pa}}$$

$$TP^{(1-\gamma)/\gamma} = \text{const.} \quad : \quad T_iP_i^{(1-\gamma)/\gamma} = T_f P_f^{(1-\gamma)/\gamma}$$

$$T_f = T_i\left(\frac{P_i}{P_f}\right)^{(1-\gamma)/\gamma} = 300\text{k}\left(\frac{1.01\times10^5\,\text{Pa}}{38{,}272\,\text{Pa}}\right)^{(1-7/5)/7/5} = 227.3\,\text{k}$$

$$\boxed{T_f = 227\text{k}}$$

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Question 2

Answer either part a) or part b) for full credit for this problem.

a) Consider a system for which the energy is $E = \alpha V T^4$ and $P = \frac{1}{3}\alpha T^4$. Determine expressions for

$$\left(\frac{\partial E}{\partial V}\right)_P \quad \text{and} \quad \left(\frac{\partial E}{\partial P}\right)_V .$$

$E(V,P) = 3PV$: $\boxed{\left(\frac{\partial E}{\partial V}\right)_P = 3P}$

$E(P,V) = 3PV$: $\boxed{\left(\frac{\partial E}{\partial P}\right)_V = 3V}$

Question 2 continued . . .

b) The enthalpy of a gas is $H = E + PV$. Starting with the infinitesimal version of the first law $\mathrm{d}E = \delta Q + \delta W$ show that the heat capacity at constant pressure is

$$c_P = \left(\frac{\partial H}{\partial T}\right)_P .$$

$$dH = dE + PdV + VdP = \delta Q + \delta W + PdV + VdP = TdS - \cancel{PdV} + \cancel{PdV} + VdP$$

$$dH = TdS + VdP, \quad dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$$

$$dH = T\left(\frac{\partial S}{\partial T}\right)_P dT + \left(T\left(\frac{\partial S}{\partial P}\right)_T + V\right) dP, \quad dS = \frac{C_P}{T} dT \quad \therefore \quad \frac{\partial S}{\partial T} = \frac{C_P}{T}$$

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP$$

$$\left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP = T\overbrace{\left(\frac{\partial S}{\partial T}\right)_P}^{\frac{C_P}{T}} dT + \left(T\left(\frac{\partial S}{\partial P}\right)_T + V\right) dP$$

$$\left(\frac{\partial H}{\partial T}\right)_P = T \cdot \frac{C_P}{T} \quad \therefore \quad \boxed{C_P = \left(\frac{\partial H}{\partial T}\right)_P}$$

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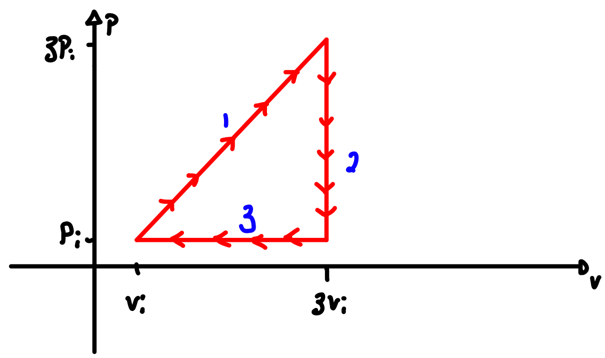
Question 3

A monoatomic ideal gas undergoes a cyclic process with the following stages, starting at initial pressure P_i and volume V_i. First it expands, during which $P = V$ at all times, until the volume reaches three times the initial volume. Second, the pressure drops back to the original pressure while the volume remains constant. Finally it is compressed back to its initial volume while the pressure remains constant.

a) Sketch the process on a PV diagram.



b) Determine an expression for the work done in each stage.

W= - Area under curve

$W_1 = -\frac{1}{2}(2P_i)(2V_i) - (P_i)(2V_i) = -2P_iV_i - 2P_iV_i = -4P_iV_i$

$W_2 = 0$

$W_3 = -(P_i)(-2V_i) = 2P_iV_i$

$$\boxed{W_1 = -4P_iV_i, \ W_2 = 0, \ W_3 = 2P_iV_i}$$

Question 3 continued . . .

c) Determine an expression for the heat added in each stage.

$\Delta E = Q + W$, $Q = \Delta E - W$, $\Delta E = \frac{3}{2}\Delta(PV)$

$Q_1 = \Delta E_1 - W_1 = \frac{3}{2}(9P_iV_i - P_iV_i) + 4P_iV_i = \frac{3}{2}\cdot 8P_iV_i + 4P_iV_i = 16P_iV_i$

$Q_2 = \Delta E_2 - \cancel{W_2}^{\,0} = \frac{3}{2}(3P_iV_i - 9P_iV_i) = \frac{3}{2}(-6P_iV_i) = -9P_iV_i$

$Q_3 = \Delta E_3 - W_3 = \frac{3}{2}(P_iV_i - 3P_iV_i) - 2P_iV_i = -3P_iV_i - 2P_iV_i = -5P_iV_i$

$$\boxed{Q_1 = 16P_iV_i \, , \; Q_2 = -9P_iV_i \, , \; Q_3 = -5P_iV_i}$$

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Question 4

An inventor claims to have produced a heat engine that uses a gas. In each cycle 1000 J of heat is supplied to the engine and the engine does 750 J of work. The lowest temperature during the engine cycle is 300 K.

a) Determine the efficiency of the engine.

$$\eta \leq \left| \frac{W_{net}}{Q_{+}} \right| \leq \left| \frac{750 J}{1000 J} \right| \leq 0.75$$

$$\boxed{\eta \leq 0.75}$$

b) Determine the minimum value of the temperature of the high temperature reservoir needed to run this engine.

$$\eta \leq 1 - \frac{T_L}{T_H} \quad : \quad \eta - 1 \leq - \frac{T_L}{T_H} \quad : \quad \frac{T_L}{T_H} \leq 1 - \eta \quad \therefore \quad T_H \geq \frac{T_L}{1-\eta}$$

$$T_H \geq \frac{300 k}{1 - 3/4} \geq 4 (300 k) \geq 1200 k$$

$$\boxed{T_H \geq 1200 k}$$

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Question 5

Answer either part a) or part b) for full credit for this problem.

a) The entropy of a monoatomic ideal gas is

$$S(T,V) = \frac{3}{2}Nk\ln(T) + Nk\ln(V) + g(N)$$

where $g(N)$ is an unknown function of N. This gas undergoes a free expansion. Determine whether ΔS is positive, negative or zero. Determine whether the change in Gibbs free energy is positive, negative or zero.

$\Delta T = 0 \quad \therefore \quad \Delta S = Nk\ln(V_F) - Nk\ln(V_i) = Nk\ln(V_F/V_i)$

$V_F > V_i \quad \therefore \quad \ln(V_F/V_i) > 0 \quad \therefore \quad \Delta S > 0$

$\Delta G = \Delta E + P\Delta V - T\Delta S = \cancel{\frac{3}{2}Nk\Delta T}^{0} + \cancel{\frac{3}{2}Nk\Delta T}^{0} - T\Delta S \quad : \quad \Delta S > 0 \quad \therefore \quad \Delta G < 0$

Question 5 continued ...

b) Use the Helmholtz free energy to show that, for a gas,

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T.$$

$F = E - TS \;:\; dF = dE - Tds - SdT \quad , \quad dE = Tds - PdV$

$dF = \cancel{Tds} - Pdv - \cancel{Tds} - SdT \;:\; dF = -Pdv - SdT$

$dF = \left(\frac{\partial F}{\partial v}\right)_T dv + \left(\frac{\partial F}{\partial T}\right)_V dT$

$\left(\frac{\partial F}{\partial v}\right)_T dv + \left(\frac{\partial F}{\partial T}\right)_V dT = -Pdv - SdT$

$P = -\left(\frac{\partial F}{\partial V}\right)_T \quad , \quad S = \left(\frac{\partial F}{\partial T}\right)$

$\left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial^3 F}{\partial T \partial v}\right) \quad , \quad \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial^2 F}{\partial v \partial T}\right) \;:\; \frac{\partial^2 F}{\partial T \partial v} = \frac{\partial^2 F}{\partial v \partial T} \;\therefore$

$$\boxed{\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial P}\right)_T}$$

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Question 6

An ideal gas undergoes a compression at constant pressure.

a) Which of the following is true regarding the change in entropy of the gas?

i) $\Delta S_{\text{gas}} = 0$.
ii) $\Delta S_{\text{gas}} < 0$.
iii) $\Delta S_{\text{gas}} > 0$.

b) Which of the following is true regarding the magnitude of the change in entropy of the environment?

i) $|\Delta S_{\text{env}}| = |\Delta S_{\text{gas}}|$.
ii) $|\Delta S_{\text{env}}| < |\Delta S_{\text{gas}}|$.
iii) $|\Delta S_{\text{env}}| > |\Delta S_{\text{gas}}|$.

Briefly explain your answers.

$\frac{T_i}{V_i} = \frac{T_F}{V_F} \to T_F = T_i \cdot \frac{V_F}{V_i} < 1 \therefore T_F < T_i \therefore \Delta T = 0$

$\Delta S = \frac{mc\Delta T}{T} \to < 0$ beause $\Delta T < 0$

Because not adiabatic $\Delta S_{Tot} \neq 0$, $\Delta S_E > \Delta S_G$

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